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317

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<p>(21) International Application Number: PCT/US93/03378</p> <p>(22) International Filing Date: 9 April 1993 (09.04.93)</p> <p>(30) Priority data: 868,920 15 April 1992 (15.04.92) US</p> <p>(71) Applicant: EXXON CHEMICAL PATENTS INC. [US/ US]; 1900 East Linden Avenue, Linden, NJ 07036 (US).</p> <p>(72) Inventors: BLOCH, Ricardo ; 1532 Ashbrook Drive, Scotch Plains, NJ 07076 (US). RITCHIE, Andrew, James, Dalviel ; 83 Canterbury Road, Chatham, NJ 07928 (US). RYER, Jack ; 61 Jensen Street, East Brun- swick, NJ 08816 (US).</p>		<p>(74) Agent: ALLEN, Mary, M.; Exxon Chemical Company, P.O. Box 710, Linden, NJ 07036 (US).</p> <p>(81) Designated States: AU, BR, CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report.</i></p>
<p>(54) Title: LUBRICANT COMPOSITION CONTAINING MIXED FRICTION MODIFIERS</p> <p>(57) Abstract</p> <p>The present invention provides an improved lubricating oil composition for automotive internal combustion engines and transmission which comprises an oil of lubricating viscosity having admixed therewith a minor amount of friction modifier composition which reduces the coefficient of friction between moving mechanical parts, thereby providing for enhanced fuel economy. The friction modifier composition comprises a combination of an alkoxylated hydrocarbyl amine or a boronated derivative thereof and hydrocarbyl phenol sulfide. This combination of components provides for synergistic fuel economy effects particularly when used as components in automotive crankcase lubricants also containing conventional additive packages, which effects are not observed in oil which contains one or the other of these components alone.</p>		

LUBRICANT COMPOSITION CONTAINING MIXED FRICTION MODIFIERSBACKGROUND OF THE INVENTION1. Field of the Invention

This invention relates to lubricating oil compositions which exhibit enhanced fuel economy and which contain a minor amount of the friction modifier combination of an alkylated phenol sulfide and an alkoxylated hydrocarbyl amine.

2. Description of Related Art

It is an objective of the automotive and oil industry to provide lubricating oil compositions which exhibit improvements in fuel savings in gasoline and diesel engine vehicles. In order to meet these goals, additives have been developed for crankcase and transmission oils which significantly reduce friction between engine or transmission moving parts, which reduction translates into improved mileage per volume of fuel consumed by an internal combustion engine. Because modern day lubricating oil compositions are complex formulations, such additives must be compatible with other components present in the oil and should not adversely affect the numerous other functions of conventional lubricant additives such as

dispersancy, viscosity stability, corrosion, oxidation inhibition and the like.

Representative examples of known oil additive modifiers are found in U.S. Patent No. 3,933,659 which discloses fatty acid esters and amides; U.S. Patent No. 4,176,074 which describes molybdenum complexes of polyisobutenyl succinic anhydride-amino alkanols; U.S. Patent 4,105,571 which discloses glycerol esters of dimerized fatty acids; U.S. Patent No. 3,779,928 which discloses alkane phosphonic acid salts; U.S. Patent No. 3,778,375 which discloses reaction products of a phosphonate and oleamide; U.S. Patent No. 3,852,215 which discloses S-carboxy-alkylene hydrocarbyl succinimide, S-carboxyalkylene hydrocarbyl succinic acid and mixtures thereof; U.S. Patent 3,879,306 which discloses N-(hydroxy-alkyl) alkenyl-succinamic acids or succinimides; U.S. Patent No. 3,932,290 which discloses reaction products of di-(lower alkyl) phosphites and epoxides; and U.S. Patent No. 4,028,258 which discloses the alkylene oxide adduct of phosphosulfurized N-(hydroxyalkyl) alkenyl succinimides.

Another known category of friction modifiers includes alkoxyated hydrocarbyl mono or polyamines such as generally illustrated by formulas 1 and 2 below. These amines include materials such as N,N-bis(2-hydroxyalkyl) hydrocarbyl amines such as disclosed in U.S. Patents 3,711,406, 3,796,662, 3,933,659, 4,010,106, 4,129,508, 4,170,560, 4,231,883 and 4,795,583.

In addition, U.S. Patent 4,086,172 discloses an additive combination for lubricating oils comprising a mixture of an oil soluble hydroxy amine such as an alkoxyated fatty amine and an oil soluble antioxidant component such as an aromatic sulfide. The mixture is said to impart improved antioxidant properties into the oil.

U.S. Patent 4,938,880 discloses lubricant compositions which may contain a metal salt of a phenol sulfide and a friction modifier.

U.S. Patent 4,764,294 discloses a lubricating oil additive combination comprising a metal phosphate, a metal carbamate and an alkyl hydroxyl aryl sulfide (nonyl phenol sulfide). The combination of these three additives is said to provide a synergistic improvement in imparting anti-wear and friction reducing properties.

U.S. Patent 4,587,026 discloses an oil additive useful for friction reduction and improved stability. This additive is an amine sulfurized concentrate prepared by forming the reaction product of an alkylated phenol sulfide, a boron-containing compound and an alkoxyated amine which may include bis(2-hydroxy ethyl) oleamide. The evident structure of the reaction product is shown in claim 22 of this patent.

The present invention is based on the discovery that a combination of one or more alkoxyated hydrocarbylamines and one or more alkylated phenol sulfides, as defined herein, added to lubricating oil compositions in specific proportions imparts a

more enhanced friction modifying property to the lubricant than an equivalent quantity of either component alone.

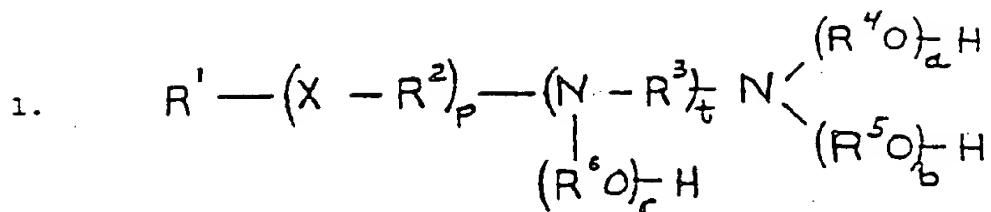
SUMMARY OF THE INVENTION

The present invention provides an improved lubricating oil composition for automotive internal combustion engines and transmissions which comprises an oil of lubricating viscosity having admixed therewith a minor amount of friction modifier composition which reduces the coefficient of friction between moving mechanical parts, thereby providing for enhanced fuel economy. The friction modifier composition comprises a combination of an alkoxyated hydrocarbyl amine and an alkylated phenol sulfide. This combination of components provides for synergistic fuel economy effects, particularly when used as components in automotive crankcase lubricants also containing conventional additive packages, which effects are not observed in oil which contains one or the other of these components alone.

DETAILED DESCRIPTION

The alkoxyated amines which are suitable as one component of the friction modifier composition of

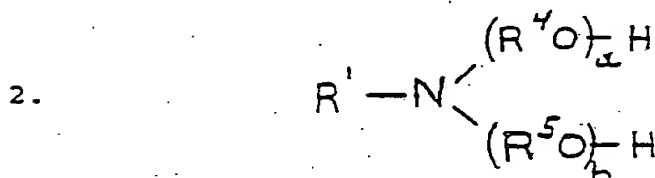
this invention have the general formula 1:



and also includes boronated derivatives thereof, wherein R^1 is a branched or straight chain hydrocarbyl group containing from about 8 to about 30 carbon atoms, R^2 and R^3 are independently the same or different branched or straight chain alkylene radicals containing 1 to 6 carbon atoms, R^4 , R^5 and R^6 are independently the same or different alkylene radicals containing from 2 to 4 carbon atoms, X is oxygen or sulfur, p is 0 or an integer ranging from 1 to 20, t is independently 0 or 1, and a, b and c are independently integers ranging from 1 to 4. In the more preferred embodiment, R^1 is a saturated or ethylenically unsaturated hydrocarbyl group containing from 12 to 24 carbon atoms, R^2 and R^3 independently contain 2-4 carbon atoms, R^4 , R^5 and R^6 independently contain 2 or 3 carbon atoms, X is oxygen and a, b and c are independently integers of 1 or 2. In the above formula, both p and t may be 1 or either p or t may be 1 when the other of them is 0, or p may be 1-20 when t is 0.

6

In the most preferred embodiment, the alkoxyated amine is a monoamine subgenus of formula 1, where p and t are each 0, having the formula 2:



wherein R^1 , R^4 , R^5 , a and b are as set forth above.

In the most preferred embodiment of the invention as set forth in formula 2, R^1 is a saturated or ethylenically unsaturated hydrocarbyl group having from 12 to 24 carbon atoms, particularly a group derived from tallow amine, oleyl amine, stearyl amine, lauryl amine, behnyl amine and the like as well as mixtures thereof, R^4 and R^5 each contain 2 or 3 carbon atoms, and $a = b = 1$.

Illustrative of more preferred alkoxyated amines within the scope of this invention include N,N',N'-tri(2-hydroxyethyl) N-octadecyl propylene diamine, N,N',N'-tri(2-hydroxyethyl) N-octadecenyl propylene diamine, N,N',N'-tri(2-hydroxyethyl) N-hexadecyl propylene diamine, N,N',N'-tri(3-hydroxypropyl) N-octadecadienyl propylene diamine, N,N',N'-tri(2-hydroxyethyl) N-octadecyl ethylene diamine, N,N',N'-tri(2-hydroxyethyl) N-octadecenyl ethylene diamine, N,N',N'-tri(2-hydroxyethyl)

N-tetradecyl propylene diamine, N,N-di(2-hydroxyethyl) oleyl amine, N,N-di-(2-hydroxyethyl) stearyl amine, N,N-di(3-hydroxypropyl) tetradecyl amine, N,N-di(2-hydroxyethyl) octadecylamine, N,N-di(2-hydroxyethyl) eicosylamine, N,N-di(2-hydroxyethyl) tallowamine, N,N-di(2-hydroxypropyl) tallowamine, N-(2-hydroxyethyl)-N-(hydroxyethoxyethyl)-n-dodecylamine, N,N-di(2-hydroxyethyl)-1-methyl-undecylamine, N,N-di(2-hydroxyethoxyethoxyethyl)-1-ethyl-octadecylamine, N,N-di(2-hydroxyethyl)-n-dodecyloxyethylamine, N,N-di(2-hydroxyethyl)-lauryloxyethylamine, N,N-di(2-hydroxyethyl)-stearyloxyethylamine, N,N-di(2-hydroxyethyl)-n-dodecyloxypropylamine, N,N-di(2-hydroxyethyl)-stearyloxypropylamine, N,N-di(2-hydroxyethyl)-dodecylthioethylamine, N,N-di(2-hydroxyethyl)-dodecylthiopropylamine, N,N-di(2-hydroxyethyl)-hexadecylthioethylamine, N,N-di(2-hydroxyethyl)-hexadecylthiopropylamine, N-2-hydroxyethyl,N-[N',N'-bis(2-hydroxyethyl)ethylamine]-octadecylamine, N-2-hydroxyethyl,N-[N',N'-bis(2-hydroxyethyl)ethylamine]-stearylamine, and the like, as well as boronated derivatives thereof.

Illustrative of the most preferred alkoxyated amines are those of formula 2 and wherein R_4 and R^5 each have 2 carbon atoms and include:

N,N-bis(2-hydroxyethyl) tallow-amine
 N,N-bis(2-hydroxyethyl)-n-dodecylamine
 N,N-bis(2-hydroxyethyl)-1-methyl-tridecenylamine
 N,N-bis(2-hydroxyethyl)-hexadecylamine
 N,N-bis(2-hydroxyethyl)-octadecylamine

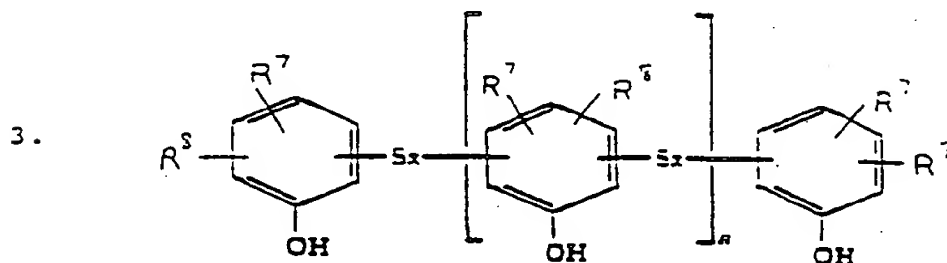
N,N-bis(2-hydroxyethyl)-octadecenylamine
N,N-bis(2-hydroxyethyl)-oleylamine
N,N-bis(2-hydroxyethyl)-stearylamine
N,N-bis(2-hydroxyethyl)-undecylamine
and boronated derivatives thereof.

The hydroxyl amine compounds may be used as such. However they may also be used in the form of an adduct or reaction product with a boron compound, such as a boric oxide, a boron halide, a metaborate, boric acid, or a mono-, di-, or triorgano borate, such as a mono-, di-, and trialkyl borate. Such adducts or derivatives may be prepared by contacting the above amines with a boronating agent. Preferred boronation agents include boric acid and boric acid esters, e.g., tributyl borate. A stoichiometric amount of the boronating agent relative to the hydroxy groups present in the amine can be used or an excess of boronating agent of up to a 50-100% excess or more can be used and is often desirable for certain applications. Thus, boronation can be complete or partial. Usually boronation levels vary from about 0.05 to about 7 weight % of boron in the boronated derivative.

Preferably the boronated derivatives are prepared in the presence of an alcoholic or hydrocarbon solvent. The presence of a solvent is not essential, however. If one is used, it may be reactive or non-reactive. Suitable non-reactive solvents include benzene, toluene, xylene and the like. Suitable reactive solvents include isopropanol, butanol, the pentanols and the like. Reaction temperatures may vary from about 70° to

about 250°C with about 110° to about 170°C being preferred.

The second essential component of the friction modifier composition of this invention is one or a mixture of hydrocarbyl phenol sulfides having the following general formula 3:



wherein R^7 and R^8 may be hydrogen or the same or different hydrocarbyl radicals containing from about 5 to 40 carbon atoms, at least one of R^7 or R^8 being a hydrocarbyl radical, x is an integer of from 1 to 4, and n is 0 or an integer of from 1 to 4. In the preferred embodiment, R^7 is an alkyl group of sufficient chain length to render the phenol sulfide compound oil soluble and preferably contains an average of from about 8 to 20 carbon atoms, n is 0, 1 or 2, preferably 0, x is 1 or 2, preferably 1 and R^8 is hydrogen. In the most preferred embodiment of this invention, R^7 is located in a position para to the hydroxyl group and sulfur is linked to the aromatic nucleus at positions ortho to the hydroxyl group.

The hydrocarbyl phenol sulfides are known materials which have been used in lubricant compositions primarily as antioxidants. They may be readily

prepared by the direct sulfurization of hydrocarbyl phenols or by reaction with a sulfur halide such as sulfur dichloride or sulfur monochloride. The reaction product generally comprises mixed phenol sulfide isomers, with the specific isomers described above forming the major component of the mixture.

The preferred phenol sulfides for use in this invention are based primarily on C_8 through C_{16} phenol monosulfides and include para nonylphenol monosulfide and para dodecylphenol monosulfide as the primary isomers.

The lubricating oil base into which the friction modifier composition of this invention may be incorporated includes automotive crankcase and transmission oils of lubricating viscosity for both diesel and gasoline engines, including natural and synthetic lubricating oils and mixtures thereof.

Natural oils include animal oils and vegetable oils such as castor oil or lard oil, liquid petroleum oils and hydrorefined oils, solvent-treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic and mixed paraffinic-naphthenic types. Oils of lubricating viscosity derived from coal or shale are also useful base oils.

Synthetic lubricating oils include hydrocarbon and halo-substituted hydrocarbon oils such as polymerized and interpolymers of olefins (e.g., polybutylenes, polypropylenes, propylene-isobutylene copolymers, chlorinated

polybutylenes, poly(1-hexenes), poly(1-octenes), poly(1-decenes); alkylbenzenes (e.g., dodecylbenzenes, tetradecylbenzenes, dinonylbenzenes, di(2-ethylhexyl) benzenes); and polyphenyls (e.g., biphenyls, terphenyls, alkylated polyphenols).

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification or etherification constitute another class of known synthetic lubricating oils. These are exemplified by polyoxylalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide, and include the alkyl and aryl ethers of these polyoxyalkylene polymers such as methyl-polyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of poly-ethylene glycol having a molecular weight of 500-1000, diethyl ether of polypropylene glycol having a molecular weight of 1000-1500, and mono-and polycarboxylic esters thereof such as acetic acid esters, mixed C_3 to C_6 fatty acid esters and the C_{13} Oxo acid diester of tetraethylene glycol.

Another suitable class of synthetic lubricating oils comprises one or more esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids and alkenyl malonic acids) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol,

2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoether and propylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, dodecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters useful as synthetic oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol and tripentaerythritol.

Silicon-based oils such as the polyalkyl, polyaryl-polyalkoxy-, or polyaryloxysiloxane oils and silicate oils comprise another useful class of synthetic lubricants. These include tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate tetra-(p-tert-butyl-phenyl) silicate, hexa-(4-methyl-2-pentoxo) disiloxane, poly(methyl)siloxanes and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid esters of phosphorus-containing acids (e.g., tricresyl phosphate, trioctyl phosphate, diethyl ester of decylphosphonic acid) and polymeric tetrahydrofurans.

Unrefined, refined and rerefined oils can be used in the lubricants of the present invention.

Unrefined oils are those obtained directly from a natural or synthetic source without further purification treatment. For example, a shale oil obtained directly from retorting operations, a petroleum oil obtained directly from distillation or ester oil obtained directly from an esterification process and used without further treatment would be an unrefined oil. Refined oils are similar to the unrefined oils except they have been further treated in one or more purification steps to improve one or more properties. Many such purification techniques, such as distillation, solvent extraction, acid or base extraction, filtration and percolation are known to those skilled in the art. Rerefined oils are obtained by processes similar to those used to obtain refined oils, but applied to refined oils which have been already used in service. Such rerefined oils are also known as reclaimed or reprocessed oils and often are additionally processed by techniques for removal of spent additives and oil breakdown products.

The components of the friction modifier composition of this invention are each blended into the lube oil base stock in amounts which reduce the friction coefficient between the mechanical parts of the engine or other apparatus in which they are used, thereby enhancing fuel economy. Generally speaking, the amount of alkoxylated amine added to the base oil will range from about 0.05 to 1.0% by weight, more preferably from about 0.1 to 0.5% by weight. The amount of hydrocarbyl phenol sulfide added to the base oil will range from about 0.1 to 2.5% by weight, more preferably from about 0.2 to

14

1.0% by weight. The preferred weight ratio of the alkoxyated amine to the phenol sulfide is in the range of from about 0.2 to 2.5:1 respectively, more preferably from about 0.4 to 1.5:1 respectively. Most preferably the phenol sulfide is present in an amount in excess of the amount of the amine, preferably at least about a 2 to 1 to 5 to 1 weight excess.

The lubricant oil of this invention is preferably also admixed with one or more additional additives to form a fully formulated oil. Such additives include dispersants, detergents, oxidation inhibitors, viscosity modifiers, corrosion inhibitors, other friction modifiers, antifoaming agents, anti wear agents and the like.

Suitable dispersants which may be employed are known in the art. A preferred class of dispersant are the ashless dispersants which are normally nitrogen-containing, oil-soluble salts, amides, imides or esters of mono or dicarboxylic acids. A particularly preferred dispersant is the reaction product of a polyolefin-substituted succinic anhydride such as polyisobutenyl succinic anhydride and an alkylene polyamine, which can be further treated with a source of boron or copper. Such a material is disclosed in U.S. Patent 4,938,880, the complete disclosure of which is incorporated herein by reference. Such dispersants are generally added to the oil in amounts ranging from about 0.1 to about 10% by weight.

Metal containing rust inhibitors and/or detergents are frequently used with ashless dispersants. Such

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detergents and rust inhibitors include the metal salts of sulphonic acids, fatty acid esters such as glycerol mono and/or di stearate (which also function as friction modifiers), alkyl phenols, sulfurized alkyl phenols, alkyl salicylates, naphthenates, and other oil soluble mono- and di-carboxylic acids. Highly basic, that is overbased metal salts, which are frequently used as detergents include calcium or magnesium phenates, sulfurized phenates and/or sulfonates. Usually these metal containing inhibitors and detergents are used in lubricating oil in amounts of about 0.01 to 10 wt. %, more preferably about 0.1 to 5 wt. %, based on the weight of the total lubricating composition. Marine diesel lubricating oils typically employ such metal-containing rust inhibitors and detergents in amounts up to about 20 wt. %.

The lube oil may also contain one or more suitable antioxidants and/or oxidation inhibitors. Suitable antioxidants include phenols, hindered phenols, bis-phenols, sulfurized phenols, catechol, alkylated and sulfurized alkylated catechols, diphenylamine, alkylated diphenylamines and phenyl-1-naphthylamines, alkyl and aryl borates, phosphites and phosphates, trialkyl and triaryl dithiophosphates and the like. Other antioxidants include oil soluble copper compounds. The copper compound may be in the cuprous and cupric form. The copper may be in the form of copper dihydrocarbyl thio- or dithio-phosphates. Alternatively the copper may be added as the copper salt of a synthetic or natural carboxylic acid. Examples include C_{10} to C_{18} fatty acids such as

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stearic or palmitic. Unsaturated acids such as oleic or branched carboxylic acids such as naphththenic acids of molecular weight from 200 to 500 or synthetic carboxylic acids are preferred because of the improved handling and solubility properties of the resulting copper carboxylates. Also useful are oil soluble copper dithiocarbamates. Copper sulphonates, phenates, and acetylacetonates may also be used. The copper antioxidant can comprise a copper salt of a hydrocarbyl substituted C_4 to C_{10} monounsaturated dicarboxylic acid producing reaction product, which reaction product is formed by reacting a polymer of a C_2 to C_{10} monoolefin having a number average molecular weight of 900 to 1400 (e.g., 700 to 1200) substituted with a C_4 to C_{10} monosaturated acid material. Exemplary are copper salts of a hydrocarbyl substituted C_4 to C_{10} monounsaturated dicarboxylic acid producing reaction product, which reaction product is formed by reacting a polymer of C_2 to C_{10} monoolefin having a number average molecular weight of from 900 to 1400 substituted with succinic moieties selected from the group consisting of acid, anhydride and ester groups, wherein there is an average of about 0.8 to 1.6 molar proportions of succinic moieties per molar proportion of the polymer.

The copper antioxidants will generally be added to the oil in an amount of from about 50-500 ppm by weight of the metal.

Corrosion inhibitors, also known as anti-corrosive agents, reduce the degradation of the metallic parts contacted by the lubricating oil composition.

Illustrative of corrosion inhibitors are phosphosulfurized hydrocarbons and the products obtained by reaction of a phosphosulfurized hydrocarbon with an alkaline earth metal oxide or hydroxide, preferably in the presence of an alkylated phenol or of an alkylphenol thioester, and also preferably in the presence of carbon dioxide. Phosphosulfurized hydrocarbons are prepared by reacting a suitable hydrocarbon such as a terpene, a heavy petroleum fraction of a C₂ to C₆ olefin polymer such as polyisobutylene, with from 5 to 30 weight percent of a sulfide of phosphorus for 0.5 to 15 hours, at a temperature in the range of 150° to 600°C. Neutralization of the phosphosulfurized hydrocarbon may be effected in the manner taught in U.S. Patent 1,969,324.

Oxidation inhibitors reduce the tendency of mineral oils to deteriorate in service which deterioration can be evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces and viscosity growth. Such oxidation inhibitors include alkaline earth metal salts of alkylphenolthioesters having preferably C₅ to C₁₂ alkyl side chains, calcium nonylphenol sulfide, barium t-octylphenyl sulfide, dioctylphenylamine, phenylalphanaphthylamine, phosphosulfurized or sulfurized hydrocarbons, etc.

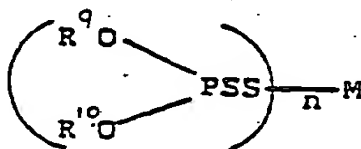
Pour point depressants lower the temperature at which the oil will flow or can be poured. Such depressants are well known. Typical of those additives which usefully optimize the low temperature fluidity of the oil are C₃-C₁₈

18

dialkylfumarate/vinyl acetate copolymers, polymethacrylates, and wax naphthalene.

Foam control can be provided by an antifoamant of the polysiloxane type, e.g. silicone oil and polydimethyl siloxane.

Another class of additive that can be included in the oil are the dihydrocarbyl dithiophosphate metal salts which are frequently used as anti-wear agents and which also provide antioxidant activity. These compounds may be generally characterized by the formula



wherein R^9 and R^{10} are each independently hydrocarbyl groups containing from 3 to about 13 carbon atoms, M is a metal and n is an integer equal to the valence of M. The hydrocarbyl groups in the phosphorodithioate structure include alkyl, cycloalkyl or alkaryl groups which may contain ether or ester linkages and which may also contain substituent groups such as halogen or nitro. Illustrative alkyl groups include isopropyl, isobutyl, n-butyl, sec-butyl, amyl, n-hexyl, methylisobutyl carbonyl, heptyl, 2-ethylhexyl, diisobutyl, isooctyl, nonyl, behenyl, decyl, dodecyl, tridecyl, etc. Illustrative lower

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19

alkylphenyl groups include xylyl, cresyl, butylphenyl, amylphenyl, heptyl-phenyl, etc. Cycloalkyl groups likewise are useful and these include chiefly cyclohexyl and the lower alkyl-cyclohexyl radicals. Many substituted hydrocarbon groups may also be used, e.g., chloropentyl, dichlorophenyl, and dichlorodecyl.

These compounds are prepared by first forming the relevant phosphorodithioic acid and then reacting this product with a suitable metal containing compound.

The phosphorodithioic acids are prepared by the reaction of phosphorus pentasulfide with an alcohol or phenol or mixtures of alcohols, mixtures of phenols or mixtures of alcohols and phenols. The reaction involves four moles of the alcohol or phenol per mole of phosphorus pentasulfide, and may be carried out within the temperature range from about 50°C to about 200°C, preferably from about 50°C to about 150°C. Thus the preparation of 0,0-di-n-hexyl phosphorodithioic acid involves the reaction of phosphorus pentasulfide with four moles of n-hexyl alcohol at about 100°C for about two hours. Hydrogen sulfide is liberated and the residue is the defined acid. The preparation of the metal salt of this acid may be effected by reaction with metal oxide. Simply mixing and heating these two reactants is sufficient to cause the reaction to take place and the resulting product is sufficiently pure for the purposes of this invention.

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The metal salts of dihydrocarbyl phosphorodithioates which are useful in this invention include those salts containing Group I metals, Group II metals, aluminum, lead, tin, manganese, cobalt, and nickel. The Group II metals, tin, iron, cobalt, lead, manganese, nickel and copper are among the preferred metals. Zinc and copper are especially useful metals. Examples of metal compounds which may be reacted with the acid include lithium oxide, lithium hydroxide, sodium hydroxide, sodium carbonate, potassium hydroxide, potassium carbonate, silver oxide, magnesium oxide, magnesium hydroxide, calcium oxide, zinc hydroxide, zinc oxide, copper oxide, strontium hydroxide, cadmium oxide, cadmium hydroxide, barium oxide, iron carbonate, copper hydroxide, lead hydroxide, tin butylate, cobalt hydroxide, nickel hydroxide, nickel carbonate and the like.

In some instances, the incorporation of certain ingredients such as small amounts of the metal acetate or acetic acid in conjunction with the metal reactant will facilitate the reaction and result in an improved product. For example, the use of up to about 5% of zinc acetate in combination with the required amount of zinc oxide facilitates the formation of a zinc phosphorodithioate.

In one preferred embodiment, the alkyl groups R^9 and R^{10} in the formula above are derived from secondary alcohols such as isopropyl alcohol, secondary butyl alcohol, 2-pentanol,

4-methyl-2-pentanol, 2-hexanol, 3-hexanol, as well as mixtures thereof.

These compounds are generally incorporated into the lubricating oil formulation in the range of from about 0.01 to about 5% by weight, more preferably from about 0.1 to about 3% by weight. The preferred compounds are the zinc dihydrocarbyl dithiophosphites.

Viscosity modifiers impart high and low temperature operability to the lubricating oil and permit it to remain relatively viscous at elevated temperatures and also exhibit acceptable viscosity or fluidity at low temperatures. Viscosity modifiers are generally high molecular weight polymers, including polyesters, polymethacrylates, polyacrylates and polyolefins. The viscosity modifiers may also be derivatized to include other properties or functions, such as the addition of dispersancy properties. These oil soluble viscosity modifying polymers will generally have number average molecular weights of from 10^3 to 10^6 , preferably 10^4 to 10^6 , e.g., 20,000 to 250,000, as determined by gel permeation chromatography or osmometry.

Examples of suitable hydrocarbon polymers include homopolymers and copolymers of two or more C_2 to C_{30} olefin monomers, e.g. C_2 to C_8 olefins, including both alpha olefins and internal olefins, which may be straight or branched, aliphatic, aromatic, alkyl-aromatic, cycloaliphatic, etc. Particularly preferred polymers are polyisobutylenes, homopolymers and copolymers of C_2 and higher alpha olefins, atactic polypropylene,

hydrogenated polymers and copolymers and terpolymers of styrene, e.g. with isoprene and/or butadiene and hydrogenated derivatives thereof. The polymer may be degraded in molecular weight, for example by mastication, extrusion, oxidation or thermal degradation, and may contain oxygen.

These viscosity modifiers are normally added to the oil composition at a level within the range of from about 0.1 to about 10% by weight.

It may also be desirable to include an additive which serves to stabilize the compatibility of lubricant compositions containing relatively high levels of friction modifiers. Examples of such additives include hydrocarbyl substituted succinic anhydrides, more preferably polyolefin-substituted succinic anhydride wherein the polyolefin has a number average molecular weight of from about 500 to 10,000, more preferably from about 1000 to 3000. Preferred polyolefin substituent groups include polyisobutylene, polybutene-1, as well as copolymers of butene-1 with ethylene and/or propylene. Polyisobutyryl succinic anhydride is a preferred compatibilizer for this purpose. This ingredient may be present in the lubricant composition at a level within the range of about 0.1 to 5% by weight, and is preferably present at about the same level as the total weight of friction modifier additives.

Compositions which contain one or more of these numerous additives are typically blended by physical admixture into the lube oil in amounts

23

effective to provide their normal attendant function.

The improved lubrication enhancement offered by compositions within the scope of this invention can be demonstrated using what is referred to as a Sequence VI Dynanometer Fuel Economy test, more specifically described as the ASTM Sequence VI test method RR: D0-2: 1204. This test is run using a 3.8 liter Buick V-6 engine equipped with cooling means to maintain a relatively constant engine oil temperature of 150°F or 275°F, coupled to a power absorbing dynanometer such that the engine speed and power output can be tightly controlled.

The lubricant to be evaluated is first flushed into the engine and aged at an oil temperature of 225 deg. F for 32 hours. The engine is then set to a specific speed and power output, and the test is conducted at the temperature for the two test stages of 150 deg. F and 275 deg. F. The engine is calibrated prior to each candidate run, using industry standard viscosity and friction modified reference oils. At each stage the average brake specific consumption is calculated. After the completion of the measurement stages, the lubricant in the engine is detergent flushed then flushed to an SAE 30 baseline oil and the measurements are repeated. These measurements are then used to calculate the Equivalent Fuel Economy Improvement (EFEI) of the candidate relative to the baseline oil.

Data reported here was collected either from the full ASTM Sequence VI test cycle or a shortened

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version of the Sequence VI test, referred to as a Sequence VI screener test, in which the test oil is aged for a reduced period of time.

The following Examples further illustrate the invention.

Examples 1-7

A base control SAE 10W-30 formulation was prepared by mixing about 94.5 parts by volume of mineral oil with effective amounts of the following additive ingredients to total 100 parts:

- Polybutenyl succinic anhydride polyamine product (borated);
- Basic Magnesium petroleum sulfonate;
- Zinc salt of mixed 2-methyl propanol, pentan-1-ol and 3-methyl butanol phosphoro dithioate;
- Oil soluble copper compound;
- Bis alkaryl amine;
- Deemulsifier
- Antifoamant
- Pour Point Depressant
- Viscosity Modifier

Taking this base control formulation, the following friction modifier ingredients were added in the following amounts by volume (V.):

Example 1: Control formulation + 0.5% V. mixed
nonyl phenol
sulfides*

25

Example 2: Control formulation + 0.2% V.
N,N-bis
(2-hydroxyethyl)
tallow amine

Example 3: Control formulation + 0.5% V. mixed
nonyl phenol
sulfides*
+ 0.2% V.
N,N-bis(2-
hydroxyethyl)
tallow amine

Example 4: Control formulation + 0.2% V.
N,N-bis(2-
hydroxypropyl)
tallow amine

Example 5: Control formulation + 0.5% V. mixed
nonyl phenol
sulfides*
+ 0.2% V. N,N-bis
(2-hydroxypropyl)
tallow amine

Example 6: Control formulation + 0.2% V. borated
N,N-bis
(2-hydroxy ethyl)
tallow amine

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Example 7: Control formulation + 0.5% V. mixed
nonyl phenol
sulfides*
+ 0.2% V. borated
N,N-bis
(2-hydroxy ethyl)
tallow amine

* 67% by weight active ingredient

The Control formulation and each of the formulations of Examples 1-7 were subjected to a Sequence VI dynamometer fuel economy screener test described above. The recorded EFEI test results are as follows:

	Recorded EFEI <u>Result</u>
Control	1.81
Example 1	1.74
Example 2	2.28
Example 3	2.65
Example 4	1.86
Example 5	2.15
Example 6	2.08
Example 7	2.91

The test results show that the mixed nonyl phenol sulfides (NPS) when added by itself at a level of 0.5% by volume to the control base formulation actually gives rise to a reduction in the EFEI test results as compared with the Control (1.74 vs. 1.81 respectively). When NPS is combined with N,N-bis

(2-hydroxyethyl) tallow amine at respective 0.5% by volume and 0.2% by volume levels as in Example 3, an EFEI test result of 2.65 is achieved which is superior to the actual EFEI value for this amine used alone at a 0.5% by volume concentration as in Example 2. In addition, since NPS used alone with the Control base formulation results in a diminution of EFEI values, the recorded EFEI results are higher than might be expected.

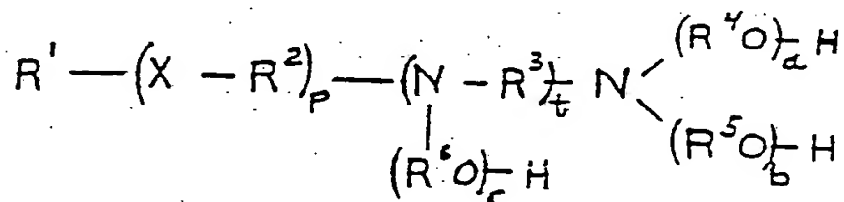
Similar unexpected results are achieved when NPS is combined with N,N-bis (2-hydroxypropyl) tallow amine as shown in Example 5 and with boronated N,N-bis (2-hydroxyethyl) tallow amine as shown in Example 7.

Thus the inclusion of the hydrocarbyl phenol sulfides of the present invention, which exhibit no friction enhancing properties on their own, into lubricating oil formulations containing an alkoxyated amine friction modifier results in a significant and synergistic enhancement of the lubricating properties of the oil.

CLAIMS:

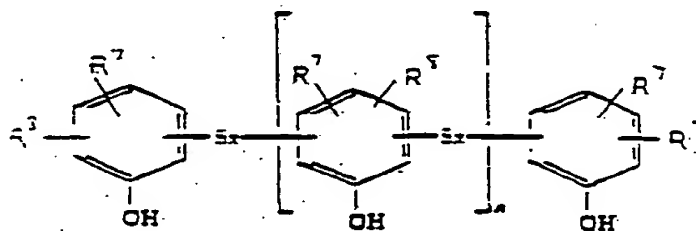
1. A lubricating oil composition comprising a major amount of an oil of lubricating viscosity having blended therewith:

- i) from about 0.05 to about 1.0% by weight of an alkoxyated amine having the formula:



wherein R^1 is a branched or straight chain hydrocarbyl group containing from about 8 to about 30 carbon atoms, R^2 and R^3 are independently the same or different branched or straight chain alkylene radicals containing 1 to 6 carbon atoms, R^4 , R^5 and R^6 are independently the same or different alkylene radicals containing from 2 to 4 carbon atoms, X is oxygen or sulfur, p is 0 or an integer ranging from 1 to 20, t is independently 0 or 1, and a , b and c are independently integers ranging from 1 to 4; and

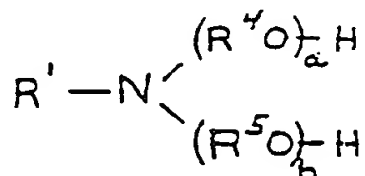
- ii) from about 0.1 to about 2.5% by weight of at least one hydrocarbyl phenol sulfide having the formula:



29

wherein R^7 and R^8 may be hydrogen or the same or different hydrocarbyl radicals containing from about 5 to 40 carbon atoms, at least one of R^7 or R^8 being a hydrocarbyl radical, x is an integer of from 1 to 4, and n is 0 or an integer of from 1 to 4.

2. The composition of claim 1 wherein said amine has the formula:



3. The composition of claim 1 wherein R^1 contains from 12 to 24 carbon atoms.

4. The composition of claim 3 wherein R^1 is tallow group.

5. The composition of claim 1 wherein each of R^4 , R^5 and R^6 contains 2 carbon atoms.

6. The composition of claim 2 wherein a and b are each 0.

7. The composition of claim 2 wherein said amine is N,N-bis(2-hydroxyethyl) tallowamine or a boronated derivative thereof.

30

8. The composition of claim 1 wherein R^7 contains an average of from about 8 to about 20 carbon atoms and R^8 is predominantly hydrogen.

9. The composition of claim 8 wherein R^7 contains an average of 9 carbon atoms.

10. The composition of claim 8 wherein n is 0.

11. The composition of claim 8 wherein x is 1.

12. The composition of claim 11 wherein said hydrocarbyl phenol sulfide is para nonyl phenol sulfide.

13. The composition of claim 2 wherein said amine comprises N,N-bis(2-hydroxyethyl) tallowamine and said sulfide comprises para nonyl phenol sulfide.

14. The composition of claim 1 wherein said amine is present in said oil at a level of from about 0.1 to about 0.5% by weight.

15. The composition of claim 14 wherein said phenol sulfide is present in said oil at a level of from about 0.2 to about 1.0% by weight.

16. The composition of claim 1 which further contains an effective amount of at least one additive selected from the group consisting of dispersants, detergents, oxidation inhibitors, viscosity modifiers, corrosion inhibitors, anti-wear agents, anti-foam agents and friction modifiers.

31

17. The composition of claim 16 wherein said additive includes a zinc dihydrocarbyldithiophosphate anti-wear agent.

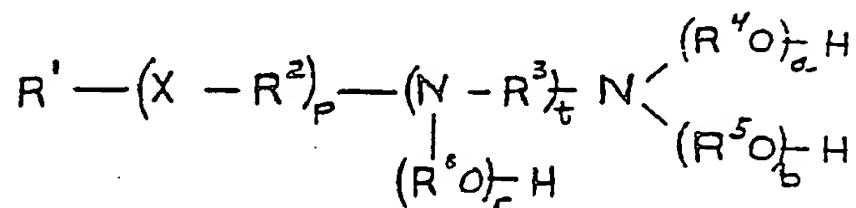
18. The composition of claim 16 wherein said additive comprises a mixture of glycerol monooleate and glycerol dioleate.

19. The composition of claim 16 wherein said additive includes a magnesium or calcium sulfonate detergent.

20. The composition of claim 16 wherein said additive includes the reaction product of a polyolefin-substituted succinic anhydride and an alkylene polyamine, or a boronated derivative thereof, as a dispersant.

21. A process for enhancing the friction properties of lubricating oil compositions comprising admixing therewith:

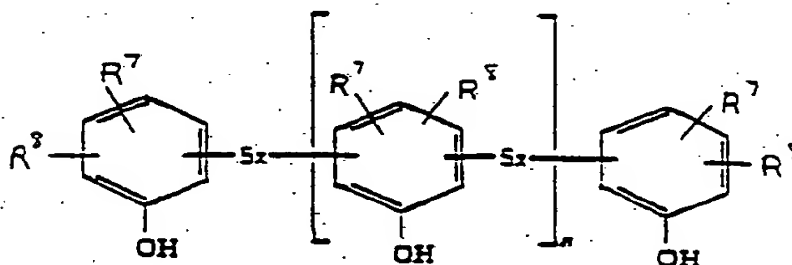
- i) from about 0.05 to about 1.0% by weight of an alkoxyated amine having the formula:



wherein R^1 is a branched or straight chain hydrocarbyl group containing from about 8 to about 30 carbon atoms, R^2 and R^3 are

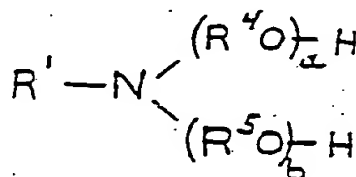
independently the same or different branched or straight chain alkylene radicals containing 1 to 6 carbon atoms, R^4 , R^5 and R^6 are independently the same or different alkylene radicals containing from 2 to 4 carbon atoms, X is oxygen or sulfur, p is 0 or an integer ranging from 1 to 20, t is independently 0 or 1, and a, b and c are independently integers ranging from 1 to 4; and

- ii) from about 0.1 to about 2.5% by weight of at least one hydrocarbyl phenol sulfide having the formula:



wherein R^7 and R^8 may be hydrogen or the same or different hydrocarbyl radicals containing from about 5 to 40 carbon atoms, at least one of R^7 or R^8 being a hydrocarbyl radical, x is an integer of from 1 to 4, and n is 0 or an integer of from 1 to 4.

22. The process of claim 21 wherein said amine has the formula:



33

23. The process of claim 22 wherein R^1 contains from 12 to 24 carbon atoms, R^4 and R^5 contain 2 carbon atoms, and a and b are each 1.

24. The process of claim 23 wherein R^7 is nonyl, x is 1 and n is 0.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/03378

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C10M141/08; C10M141/12; C10M163/00; C10M167/00 //(C10M141/08,133:08,135:30)(C10M141/12,135:30,139:00)											
II. FIELDS SEARCHED <div style="text-align: center; border: 1px solid black; padding: 2px; margin: 5px 0;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 30%; border: 1px solid black; padding: 2px;">Classification System</th> <th style="width: 70%; border: 1px solid black; padding: 2px;">Classification Symbols</th> </tr> <tr> <td style="border: 1px solid black; padding: 5px;">Int.Cl. 5</td> <td style="border: 1px solid black; padding: 5px;">C10M</td> </tr> </table> <div style="text-align: center; border: 1px solid black; padding: 2px; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched⁸</div>			Classification System	Classification Symbols	Int.Cl. 5	C10M					
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Int.Cl. 5	C10M										
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 10%; border: 1px solid black; padding: 2px;">Category¹⁰</th> <th style="width: 70%; border: 1px solid black; padding: 2px;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 20%; border: 1px solid black; padding: 2px;">Relevant to Claim No.¹³</th> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="border: 1px solid black; padding: 5px;"> US,A,4 587 026 (A.G HORODYSKY) 6 May 1986 cited in the application see column 2, line 19 see column 2, line 50 see column 4; example 1 --- </td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;"> 1-6, 8-12, 21-24 </td> </tr> <tr> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;">A</td> <td style="border: 1px solid black; padding: 5px;"> EP,A,0 314 843 (UNION OIL COMPANY OF CALIFORNIA) 10 May 1989 see page 16, line 54 see page 18, line 25 - line 26 see page 19; example 2 --- <div style="text-align: right; margin-top: 10px;">-/--</div> </td> <td style="border: 1px solid black; text-align: center; vertical-align: top; padding: 5px;"> 1-7, 21-23 </td> </tr> </table> <div style="font-size: small; margin-top: 10px;"> <div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>¹⁰ Special categories of cited documents : 10</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div> </div>			Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	US,A,4 587 026 (A.G HORODYSKY) 6 May 1986 cited in the application see column 2, line 19 see column 2, line 50 see column 4; example 1 ---	1-6, 8-12, 21-24	A	EP,A,0 314 843 (UNION OIL COMPANY OF CALIFORNIA) 10 May 1989 see page 16, line 54 see page 18, line 25 - line 26 see page 19; example 2 --- <div style="text-align: right; margin-top: 10px;">-/--</div>	1-7, 21-23
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IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search <div style="text-align: center; font-weight: bold; margin-top: 10px;">21 JULY 1993</div> </td> <td style="width: 50%; border: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold; margin-top: 10px;">02.08.93</div> </td> </tr> <tr> <td style="border: 1px solid black; padding: 5px;"> International Searching Authority <div style="text-align: center; font-weight: bold; margin-top: 10px;">EUROPEAN PATENT OFFICE</div> </td> <td style="border: 1px solid black; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center; font-weight: bold; margin-top: 10px;">HILGENGA K.J.</div> </td> </tr> </table>			Date of the Actual Completion of the International Search <div style="text-align: center; font-weight: bold; margin-top: 10px;">21 JULY 1993</div>	Date of Mailing of this International Search Report <div style="text-align: center; font-weight: bold; margin-top: 10px;">02.08.93</div>	International Searching Authority <div style="text-align: center; font-weight: bold; margin-top: 10px;">EUROPEAN PATENT OFFICE</div>	Signature of Authorized Officer <div style="text-align: center; font-weight: bold; margin-top: 10px;">HILGENGA K.J.</div>					
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III. DOCUMENTS CONSIDERED TO BE RELEVANT

(CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	<p>US,A,4 170 560 (W. LOWE) 9 October 1979</p> <p>see column 4, line 21 - line 22 see column 4, line 43 - line 61 see column 5, line 11 - line 12 see column 6, line 30 - line 33</p> <p>---</p>	<p>1-7,14, 16,17, 19,20</p>
A	<p>US,A,3 933 659 (R.E LYLE) 20 January 1976 cited in the application</p> <p>*Whole document *</p> <p>---</p>	<p>1-3,5,6, 14,16, 17,20, 21,22,23</p>
A	<p>EP,A,0 353 854 (EXXON CHEMICAL PATENTS) 7 February 1990</p> <p>see page 9, line 25 - line 46 see page 10, line 39 - line 41 see page 14, line 47 see page 15, line 20 - line 21 see page 19, line 34 - line 35 see page 21, line 11</p> <p>---</p>	<p>1,7,14, 16,17, 19,20,21</p>
A	<p>WO,A,9 202 602 (EXXON CHEMICAL PATENTS) 20 February 1992 see page 22, line 14 - line 16</p> <p>---</p>	<p>18</p>
A	<p>US,A,5 019 286 (G. SHAW) 28 May 1991 see column 1, line 7 - line 9 see column 9, line 30 - line 45 see column 9, line 56</p> <p>-----</p>	

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9303378
SA 73029

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4587026	06-05-86	None	
EP-A-0314843	10-05-89	None	
US-A-4170560	09-10-79	US-A- 4086172	25-04-78
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		GB-A- 1522963	31-08-78
		GB-A- 1522961	31-08-78
		JP-A- 51031369	17-03-76
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WO-A-9202602	20-02-92	None	
US-A-5019286	28-05-91	EP-A- 0448238	25-09-91

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